

1. A viscosifying and fluid loss controlling additive for use in well cement
5 slurries subject to temperatures up to 500°F comprising a mixture of a polymer
comprised of at least one monomer which is calcium tolerant, anionic and disperses basic
cement slurries, at least one monomer which hydrolyzes in basic cement slurries to
generate anionic carboxylate groups that bind with calcium and viscosify the slurries and
at least one monomer which generates non-ionic pendant groups on the polymer upon
10 hydrolyzing in basic cement slurries to prevent polymer precipitation and a homopolymer
of a monomer which hydrolyzes in basic cement slurries to generate anionic carboxylate
groups that bind with calcium, viscosify the slurries and prevent settling in the slurries.

2. The viscosifying and fluid loss controlling additive of claim 1 wherein
15 said monomer which is calcium tolerant, anionic and disperses basic cement slurries is
selected from the group consisting of 2-acrylamido-2-methylpropane sulfonic acid and its
salts; vinyl sulfonate, allylsulfonate and 3-allyloxy-2-hydroxy-1-propane sulfonic acid
and its salts.

20 3. The viscosifying and fluid loss controlling additive of claim 1 wherein
said monomer which is calcium tolerant, anionic and disperses basic cement slurries is 2-
acrylamido-2-methylpropane sulfonic acid or its salts.

4. The viscosifying and fluid loss controlling additive of claim 1 wherein said monomer which hydrolyzes in basic cement slurries to generate anionic carboxylate groups which bind with calcium and viscosify the slurries is selected from the group consisting of acrylonitrile, acrylamide, N,N-dialkylacrylamide wherein the alkyl group is selected from C₁ to C₆ alkyl groups, N-vinylpyrrolidone, 2-acrylamido-2-methylpropane sulfonic acid and its salts, alkylacrylate wherein the alkyl group is selected from C₁ to C₆ alkyl groups and alkylmethacrylate wherein the alkyl group is selected from C₁ to C₆ alkyl groups.

10 5. The viscosifying and fluid loss controlling additive of claim 1 wherein said monomer which hydrolyzes in basic cement slurries to generate anionic carboxylate groups which bind with calcium and viscosify the slurries is acrylamide.

15 6. The viscosifying and fluid loss controlling additive of claim 1 wherein said monomer which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation is selected from the group consisting of N-alkyl-N-vinyl-acetamide wherein the alkyl group is selected from C₁ to C₆ alkyl groups, allyl glycidyl ether and vinylacetate.

20 7. The viscosifying and fluid loss controlling additive of claim 1 wherein said monomer which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation is N-alkyl-N-vinyl-acetamide.

8. The viscosifying and fluid loss controlling additive of claim 1 wherein said monomer which is calcium tolerant, anionic and disperses basic cement slurries is present in said polymer in an amount in the range of from about 30% to about 60% by weight of said polymer.

5

9. The viscosifying and fluid loss controlling additive of claim 1 wherein said monomer which hydrolyzes in basic cement slurries to generate anionic carboxylate groups which bind with calcium and viscosify the slurries is present in said polymer in an amount in the range of from about 20% to 60% by weight of said polymer.

10

10. The viscosifying and fluid loss controlling additive of claim 1 wherein said monomer which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation is present in said polymer in an amount in the range of from about 0 to 40% by weight of said polymer.

15

11. The viscosifying and fluid loss controlling additive of claim 1 wherein said polymer is present in said mixture of said polymer and said homopolymer in an amount in the range of from about 50% to about 95% by weight of said mixture and said homopolymer is present therein in an amount in the range of from about 5% to about 50% by weight of said mixture.

20

12. The viscosifying and fluid loss controlling additive of claim 1 wherein the molecular weight of said polymer is in the range of from about 300,000 to about 1.5 million and the molecular weight of said homopolymer is in the range of from about 900,000 to about 1.5 million.

5

~~13.~~ A well cement composition for use at temperatures up to about 500°F comprising:

a hydraulic cement;

water present in an amount sufficient to form a slurry; and

10

a viscosifying and fluid loss controlling additive comprising a mixture of a polymer comprised of at least one monomer which is calcium tolerant, anionic and disperses basic cement slurries, at least one monomer which hydrolyzes in basic cement slurries to generate anionic carboxylate groups that bind with calcium and viscosify the slurries and at least one monomer which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation and a homopolymer of a monomer which hydrolyzes in basic cement slurries to generate anionic carboxylate groups that bind with calcium, viscosify the slurries and prevent settling in the slurries.

15

20

14. The cement composition of claim 13 wherein said hydraulic cement is selected from the group consisting of Portland cements, pozzolana cements, gypsum cements, aluminous cements and silica cements.

15. The cement composition of claim 13 wherein said hydraulic cement is Portland cement.

16. The cement composition of claim 13 wherein said water is selected from
5 the group consisting of fresh water, unsaturated salt solutions and saturated salt solutions.

17. The cement composition of claim 13 wherein said water is present in said composition in an amount in the range of from about 38% to about 70% by weight of said hydraulic cement therein.

10

18. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which is calcium tolerant, anionic and disperses basic cement slurries is selected from the group consisting of 2-acrylamido-2-methylpropane sulfonic acid and its salts; vinyl sulfonate, allylsulfonate and 3-allyloxy-2-
15 hydroxy-1-propane sulfonic acid and its salts.

19. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which is calcium tolerant, anionic and disperses basic cement slurries is 2-acrylamido-2-methylpropane sulfonic acid or its salts.
20

20. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which hydrolyzes in basic cement slurries to generate anionic carboxylate groups which bind with calcium and viscosify the slurries

is selected from the group consisting of acrylonitrile acrylamide, N,N-dialkylacrylamide wherein the alkyl group is selected from C₁ to C₆ alkyl groups, N-vinylpyrrolidone, 2-acrylamido-2-methylpropane sulfonic acid and its salts, alkylacrylate wherein the alkyl group is selected from C₁ to C₆ alkyl groups and alkylmethacrylate wherein the alkyl group is selected from C₁ to C₆ alkyl groups.

21. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which hydrolyzes in basic cement slurries to generate anionic carboxylate groups which bind with calcium and viscosify the slurries is acrylamide.

22. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation is selected from the group consisting of N-alkyl-N-vinyl-acetamide wherein the alkyl group is selected from C₁ to C₆ alkyl groups, allyl glycidyl ether and vinylacetate.

23. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation is N-alkyl-N-vinyl-acetamide.

24. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which is calcium tolerant, anionic and disperses basic cement slurries is present in said polymer in an amount in the range of from about 30% to about 60% by weight of said polymer.

5

25. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which hydrolyzes in basic cement slurries to generate anionic carboxylate groups which bind with calcium and viscosify the slurries is present in said polymer in an amount in the range of from about 20% to 60% by weight
10 of said polymer.

26. The cement composition of claim 13 wherein said monomer in said viscosifying and fluid loss controlling additive which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer
15 precipitation is present in said polymer in an amount in the range of from about 0 to 40% by weight of said polymer.

27. The cement composition of claim 13 wherein said polymer in said viscosifying and fluid loss controlling additive is present in the mixture of said polymer
20 with said homopolymer in an amount in the range of from about 50% to about 95% by weight of said mixture and said homopolymer is present therein in an amount in the range of from about 5% to about 50% by weight of said mixture.

28. The cement composition of claim 13 wherein said polymer in said viscosifying and fluid loss controlling additive has a molecular weight in the range of from about 300,000 to about 1.5 million and said homopolymer therein has a molecular weight in the range of from about 900,000 to about 1.5 million.

5

29. The cement composition of claim 13 wherein said viscosifying and fluid loss controlling additive is present in said cement composition in an amount in the range of from about 0.2% to about 7% by weight of hydraulic cement therein.

10 30. The cement composition of claim 13 wherein said viscosifying and fluid loss controlling additive is present in said composition in an amount of about 2% by weight of hydraulic cement therein.

15 ~~31.~~ A well cement composition for use at temperatures up to about 500°F comprising:

a hydraulic cement;

water present in an amount sufficient to form a slurry; and

a viscosifying and fluid loss controlling additive comprising a polymer having a molecular weight of about 500,000 comprised of 2-acrylamido-2-methylpropane sulfonic acid, acrylamide and N-alkyl-N-vinyl-acetamide monomers, said 2-acrylamido-2-methyl propane sulfonic acid monomer being present in said polymer in an amount in the range of from about 40% to about 50% by weight of said polymer, said acrylamide monomer being present in said polymer in an amount in the range of from about 30% to

20

about 40% by weight of said polymer and said N-alkyl-N-vinyl-acetamide being present in an amount in the range of from about 10% to about 20% by weight of said polymer and a homopolymer of acrylamide having a molecular weight of about 1 million.

5 32. The cement composition of claim 31 wherein said hydraulic cement is selected from the group consisting of Portland cements, pozzolana cements, gypsum cements, aluminous cements and silica cements.

10 33. The cement composition of claim 31 wherein said hydraulic cement is Portland cement.

 34. The cement composition of claim 31 wherein said water is selected from the group consisting of fresh water, unsaturated salt solutions and saturated salt solutions.

15 35. The cement composition of claim 31 wherein said water is present in said composition in an amount in the range of from about 38% to about 70% by weight of said hydraulic cement therein.

20 36. The cement composition of claim 31 wherein said polymer in said viscosifying and fluid loss controlling additive is present in the mixture of said polymer with said homopolymer in an amount in the range of from about 50% to about 95% by weight of said mixture and said homopolymer is present therein in an amount in the range of from about 5% to about 50% by weight of said mixture.

37. A method of cementing a subterranean zone penetrated by a well bore comprising the steps of:

- (a) providing a cement composition comprising a hydraulic cement, water present in an amount sufficient to form a slurry and a viscosifying and fluid loss controlling additive comprising a mixture of a polymer comprised of at least one monomer which is calcium tolerant, anionic and disperses basic cement slurries, at least one monomer which hydrolyzes in basic cement slurries to generate anionic carboxylate groups that bind with calcium and viscosify the slurries and at least one monomer which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation and a homopolymer of a monomer which hydrolyzes in basic cement slurries to generate anionic carboxylate groups that bind with calcium, viscosify the slurries and prevent settling in the slurries;
- (b) placing said cement composition in said subterranean zone; and
- (c) allowing said cement composition to set therein.

15

38. The method of claim 37 wherein said hydraulic cement in said composition is selected from the group consisting of Portland cements, pozzolana cements, gypsum cements, aluminous cements and silica cements.

20 39. The method of claim 37 wherein said hydraulic cement in said composition is Portland cement.

40. The method of claim 37 wherein said water in said composition is selected from the group consisting of fresh water, unsaturated salt solutions and saturated salt solutions.

5 41. The method of claim 37 wherein said water is present in said composition in an amount in the range of from about 38% to about 70% by weight of said hydraulic cement therein.

42. The method of claim 37 wherein said monomer in said viscosifying and
10 fluid loss controlling additive which is calcium tolerant, anionic and disperses basic cement slurries is 2-acrylamido-2-methylpropane sulfonic acid or its salts.

43. The method of claim 37 wherein said monomer in said viscosifying and
fluid loss controlling additive which hydrolyzes in basic cement slurries to generate
15 anionic carboxylate groups which bind with calcium and viscosify the slurries is selected from the group consisting of acrylonitrile acrylamide, N,N-dialkylacrylamide wherein the alkyl group is selected from C₁ to C₆ alkyl groups, N-vinylpyrrolidone, 2-acrylamido-2-methylpropane sulfonic acid and its salts, alkylacrylate wherein the alkyl group is selected from C₁ to C₆ alkyl groups and alkylmethacrylate wherein the alkyl group is
20 selected from C₁ to C₆ alkyl groups.

44. The method of claim 37 wherein said monomer in said viscosifying and fluid loss controlling additive which hydrolyzes in basic cement slurries to generate anionic carboxylate groups which bind with calcium and viscosify the slurries is acrylamide.

5

45. The method of claim 37 wherein said monomer in said viscosifying and fluid loss controlling additive which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation is selected from the group consisting of N-alkyl-N-vinyl-acetamide wherein the alkyl group is
10 selected from C₁ to C₆ alkyl groups, allyl glycidyl ether and vinylacetate.

46. The method of claim 37 wherein said monomer in said viscosifying and fluid loss controlling additive which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation is N-alkyl-N-
15 vinyl-acetamide.

47. The method of claim 37 wherein said monomer in said viscosifying and fluid loss controlling additive which is calcium tolerant, anionic and disperses basic cement slurries is present in said polymer in an amount in the range of from about 30% to
20 about 60% by weight of said polymer.

48. The method of claim 37 wherein said monomer in said viscosifying and fluid loss controlling additive which hydrolyzes in basic cement slurries to generate

anionic carboxylate groups which bind with calcium and viscosify the slurries is present in said polymer in an amount in the range of from about 20% to 60% by weight of said polymer.

5 49. The method of claim 37 wherein said monomer in said viscosifying and fluid loss controlling additive which generates non-ionic pendant groups on the polymer upon hydrolyzing in basic cement slurries to prevent polymer precipitation is present in said polymer in an amount in the range of from about 0 to 40% by weight of said polymer.

10

 50. The method of claim 37 wherein said polymer in said viscosifying and fluid loss controlling additive is present in the mixture of said polymer with said homopolymer in an amount in the range of from about 50% to about 95% by weight of said mixture and said homopolymer is present therein in an amount in the range of from
15 about 5% to about 50% by weight of said mixture.

 51. The method of claim 37 wherein said polymer in said viscosifying and fluid loss controlling additive has a molecular weight in the range of from about 300,000 to about 1.5 million and said homopolymer therein has a molecular weight in the range of
20 from about 900,000 to about 1.5 million.

52. The method of claim 37 wherein said viscosifying and fluid loss controlling additive is present in said cement composition in an amount in the range of from about 0.2% to about 7% by weight of hydraulic cement therein.

5 53. The method of claim 37 wherein said viscosifying and fluid loss controlling additive is present in said composition in an amount of about 2% by weight of hydraulic cement therein.

54. A method of cementing a subterranean zone penetrated by a well bore
10 comprising the steps of:

(a) providing a cement composition comprising a hydraulic cement, water present in an amount sufficient to form a slurry and a viscosifying and fluid loss controlling additive comprising a polymer having a molecular weight of about 500,000 comprised of 2-acrylamido-2-methylpropane sulfonic acid, acrylamide and N-alkyl-N-
15 vinyl-acetamide monomers, said 2-acrylamido-2-methyl propane sulfonic acid monomer being present in said polymer in an amount in the range of from about 40% to about 50% by weight of said polymer, said acrylamide monomer being present in said polymer in an amount in the range of from about 30% to about 40% by weight of said polymer and said N-alkyl-N-vinyl-acetamide being present in an amount in the range of from about 10% to
20 about 20% by weight of said polymer and a homopolymer of acrylamide having a molecular weight of about 1 million;

(b) placing said cement composition in said subterranean zone; and

(c) allowing said cement composition to set therein.

55. The method of claim 54 wherein said hydraulic cement is selected from the group consisting of Portland cements, pozzolana cements, gypsum cements, aluminous cements and silica cements.

5 56. The method of claim 54 wherein said hydraulic cement is Portland cement.

57. The method of claim 54 wherein said water is selected from the group consisting of fresh water, unsaturated salt solutions and saturated salt solutions.

10

58. The method of claim 54 wherein said water is present in said composition in an amount in the range of from about 38% to about 70% by weight of said hydraulic cement therein.

15 59. The method of claim 54 wherein said polymer in said viscosifying and fluid loss controlling additive is present in the mixture of said polymer with said homopolymer in an amount in the range of from about 50% to about 95% by weight of said mixture and said homopolymer is present therein in an amount in the range of from about 5% to about 50% by weight of said mixture.